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The mixed-metal nitridophosphate $Na_3TiN(PO_3)_3$

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(P–N) = 0.004 Å
R factor = 0.032
wR factor = 0.079
Data-to-parameter ratio = 7.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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The title compound, trisodium titanium nitride tris(phosphate), is built up from $Ti^{III}O_6$ octahedra linked together *via* $[N(PO_3)_3]$ groups, the latter arising from three PO_3N tetrahedra sharing an N vertex. Three sodium cations complete the structure, which is also found for $Na_3AlN(PO_3)_3$. All the metal cations and the N atom occupy special positions with site symmetry 3.

Comment

Complex phosphates display a great variety of compositions and structural types. Many double phosphates possess valuable physical characteristics, such as luminescence, ionic conductivity, segnetoelectric properties and nonlinear optical behaviour. The condensation of phosphate anions into finite and infinite polyphosphate species occurs by vertex sharing of the $[PO_4]$ tetrahedra, resulting in an enormous number of anionic forms. Even so, this way of linking phosphate tetrahedra does not exhaust all possible variants. Partial substitution of N atoms for O atoms in PO_4 tetrahedra (according to the scheme $1.5O^{2-} \equiv N^{3-}$) provides new possibilities for building 'non-classical' nitridophosphate anionic groups, which are interesting both in their fundamental and applied aspects.

Two new families of mixed-metal nitridophosphates of the types $M^I_3M^{III}[NP_3O_9]$ and $M^I_2M^{II}_2[NP_3O_9]$ (M^I = Na and K; M^{III} = Al, Cr, Ga, V and Ti; M^{II} = Mg) were obtained by solid-state techniques (Feldmann, 1987*a*,*b*). Later, a single-crystal X-ray study of $Na_3AlN(PO_3)_3$ (Conanec *et al.*, 1994) and a solid-state NMR study of $Na_2Mg_2N(PO_3)_3$ (Massiot *et al.*, 1996) were reported. The lack of further work on these unusual compounds can be explained by the difficulties in the preparation of pure crystalline samples.

We report here the flux-growth synthesis and structural characterization of the title compound, (I), $Na_3TiN(PO_3)_3$. Its cubic non-centrosymmetric structure (space group $P2_13$) is the same as that of $Na_3AlN(PO_3)_3$ (Conanec *et al.*, 1994). Compound (I) contains $[N(PO_3)_3]^{6-}$ anions, connected *via* O vertices with $[Ti^{III}O_6]$ octahedra (Table 1). The TiO_6 geometry in (I) is similar to that seen in $TiPO_4$ (Glaum & Gruehn, 1992). The $[N(PO_3)_3]^{6-}$ anion in (I) is formed by three $[PO_3N]$ tetrahedra sharing an N vertex. The P—O bond lengths range from 1.499 (4) to 1.526 (4) Å, with the P—N bond much longer at 1.725 (4) Å. For comparison, the P—N bond distance in $Na_3P_6N_{11}$ (Ronis *et al.*, 1990) involving the three-coordinate-to-phosphorus N atom is 1.744 (13) Å.

Three types of Na^+ cation are present in (I). Atoms Na1 (Fig. 3) have a distorted NaO_6N capped trigonal prismatic environment with the N atom above a triangular face at a distance of 3.078 (5) Å from Na1. Atom Na2 (Fig. 4) is also

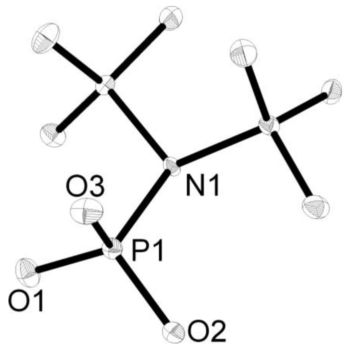

Figure 1
Detail of (I), showing the three phosphate tetrahedra linked *via* the central N atom (50% probability displacement ellipsoids).

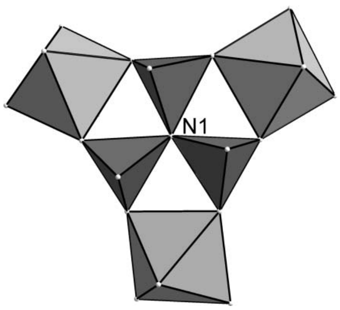

Figure 2
Linking of the $[N(PO_3)_3]^{6-}$ anion with three adjacent metal octahedra in (I).

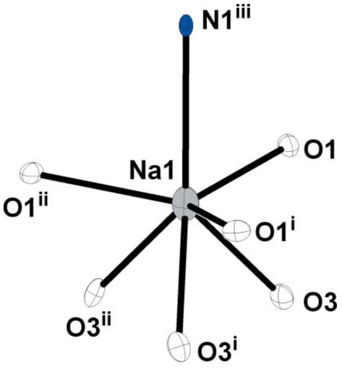

Figure 3
The coordination environment of the Na1 cation in (I) (50% probability displacement ellipsoids). [Symmetry codes: (i) $z - 1, 1 + x, y$; (ii) $y - 1, z, 1 + x$; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$.]

seven-coordinate, with six O- and one N-atom neighbours. However, its geometry is best described as distorted octahedral, with N1 [Na—N = 3.188 (4) Å] capping through an octahedral face. Atom Na3 (Fig. 5) has nine O-atom neighbours. Six of these O atoms form a very distorted trigonal antiprism with Na—O = 2.375 (5) and 3.043 (5) Å. Three slightly longer Na3—O2 bonds [3.117 (5) Å] cap the faces of the prism. Overall, a wide range of Na—O distances [2.330 (4)–3.117 (5) Å] are seen in this structure.

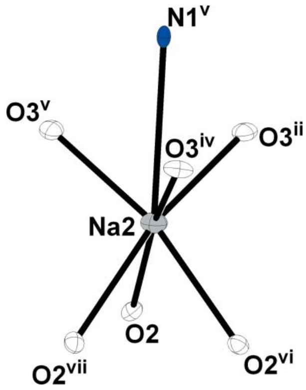

Figure 4
The coordination environment of the Na2 cation in (I) (50% probability displacement ellipsoids). [Symmetry codes: (ii) $y - 1, z, 1 + x$; (iv) $z - \frac{1}{2}, \frac{1}{2} - x, 2 - y$; (v) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (vi) $y - \frac{1}{2}, \frac{3}{2} - z, 1 - x$; (vii) $1 - z, \frac{1}{2} + x, \frac{3}{2} - y$.]

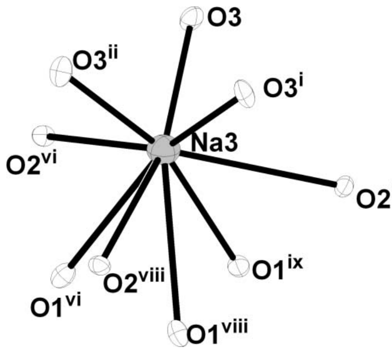

Figure 5
The coordination environment of the Na3 cation in (I) (50% probability displacement ellipsoids). [Symmetry codes: (i) $z - 1, 1 + x, y$; (ii) $y - 1, z, 1 + x$; (vi) $y - \frac{1}{2}, \frac{3}{2} - z, 1 - x$; (viii) $\frac{1}{2} - z, 1 - x, \frac{1}{2} + y$; (ix) $-x, \frac{1}{2} + y, \frac{3}{2} - z$.]

The crystal packing (Conanec *et al.*, 1994) in (I) sees the $N(PO_3)_3^{6-}$ anion bridging to three adjacent TiO_6 octahedra (Fig. 2). Along the [111] direction the sequence {N1–Na1–Na3–Ti1–Na2} occurs.

Experimental

A mixture of $NH_4H_2PO_4$ (11.3 g), Na_2CO_3 (7.3 g) and urea (17.6 g), ground in an agate mortar, was heated to full outgasing at 600 K in a porcelain dish. The resulting solid was reground and heated to melting at 1020 K. Powdered TiO_2 (0.8 g) was added, with mixing, to the melt at 980 K. The mixture was heated for 1 h at 980 K, and then cooled to 920 K at a rate of 25 K h^{-1}. After cooling to room temperature, the violet tetrahedral crystals of (I) were washed with deionized water. Elemental analysis indicated the presence of Na, Ti, P and N in the atomic ratio 3:1:3:1.

Crystal data

$Na_3TiN(PO_3)_3$
$M_r = 367.79$
Cubic, $P2_13$
$a = 9.4984$ (10) Å
$V = 856.94$ (16) Å^3
$Z = 4$
$D_x = 2.851$ Mg m^{-3}
Mo $K\alpha$ radiation

Cell parameters from 25 reflections
$\theta = 3.0$–28°
$\mu = 1.75$ mm^{-1}
$T = 298$ K
Tetrahedron, violet
0.10 × 0.10 × 0.10 mm

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Data collection

Enraf–Nonius CAD-4 diffractometer
Non–profiled $\omega/2\theta$ scans
Absorption correction: analytical (Alcock, 1970)
$T_{\min} = 0.758$, $T_{\max} = 0.812$
1209 measured reflections
409 independent reflections
338 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.075$
$\theta_{\max} = 28.0^\circ$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 12$
2 standard reflections every 122 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.079$
$S = 1.06$
409 reflections
52 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}
Absolute structure: Flack (1983), 0 Friedel pairs
Flack parameter: 0.11 (10)

Table 1
Selected geometric parameters (Å, °).

Na1—O3	2.578 (5)	Na3—O2$^{\rm ix}$	3.117 (5)
Na1—O1	2.590 (5)	Ti1—O1$^{\rm x}$	2.002 (4)
Na1—N1$^{\rm iii}$	3.078 (5)	Ti1—O2	2.015 (4)
Na2—O3$^{\rm iv}$	2.330 (4)	P1—O3	1.499 (4)
Na2—O2	2.475 (4)	P1—O2	1.520 (4)
Na2—N1$^{\rm v}$	3.188 (4)	P1—O1	1.526 (4)
Na3—O3	2.375 (5)	P1—N1	1.725 (4)
Na3—O1$^{\rm ix}$	3.043 (5)		
P1$^{\rm xi}$—N1—P1	115.35 (17)		

Symmetry codes: (iii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iv) $z-\frac{1}{2}, -x+\frac{1}{2}, -y+2$; (v) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (ix) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (x) $z, x+1, y$; (xi) $-y+1, z+\frac{1}{2}, -x+\frac{1}{2}$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *PROFIT* (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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